3

CRYSTAL BONDING

Crystal Bonding :

The ability to hold the atoms or ions together is called bonding.

Types of bonding:

The individual atoms of a crystalline solid are held together as one system with different types of bonds existing between them. These bonds are classified into five idealised types.

(i) Ionic bonding : Ionic bond is formed by the complete transfer of electrons from electropositive atom to an electronegative atom.

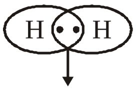
Example : NaCl. Na atom has 11 electrons and Cl atom has 17 electrons. Bond in NaCl crystal is formed by complete transfer of an electron from Na to Cl.

$$\overset{\curvearrowright}{\underset{11}{\mathrm{Na}}\qquad\underset{17}{\mathrm{Cl}}} \longrightarrow \mathrm{Na}^{+}-\mathrm{Cl}^{-}$$

“Ionic bond is formed between electropositive and electronegative atoms”. This bond has spherically symmetric charge distribution. Hence, it is not directional in nature.

(ii) Covalent bonding : Covalent bond is formed by sharing of electrons between two atoms

Examples: H_2, diamond, SiC.



Localized (bound)

In this type of bonding, charge distribution is not spherically symmetric. Charge density is maximum in the direction of bond formation. Hence, this bond is highly directional in nature.

(iii) Metallic bonding : This type of bond is also formed by sharing of electrons but shared electron pair is not localized. Shared electron pair can move within the solid.

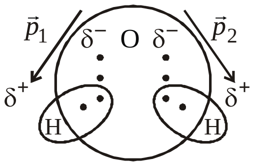
Examples: Cu, Ag, Fe, Na, Li, Au etc.

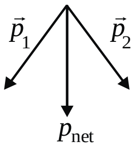
(iv) Van der Waal bonding : This type of bonding is generally formed between those atoms or molecules which do not have tendency to share or transfer electrons among them. Van der waal bonding is very weak bonding. This bonding arises due to induced dipole moment. This is slightly directional.

Examples: Inert gases like He, Ne, Ar, solid Argon.

(v) Hydrogen bonding : When a covalent bond is formed between Hydrogen atom and any highly electronegative atom like oxygen, Cl, etc. then shared electron pair is attracted more towards the electronegative atom. This causes the formation of permanent dipole.

Example: H_2O.





Permanent electric dipole moment is the source of H-bonding.

The reason of H-bonding is bond formation between highly electronegative atom and hydrogen. This bond is also directional in nature.

Interatomic forces :

There exist interatomic forces between the atoms of crystal that hold the atoms to form crystalline structure. From the very existence of solids, two general conclusions can be drawn.

(i) There is an attractive force between atoms or molecules in a solid which keeps them together,

(ii) There is a repulsive force acting between the atoms. This is why large external pressure is required to compress a solid to any appreciable extent.

When two identical or non-identical atoms, which form a molecule, are brought from infinity to a close proximity, they first attract each other and then, if they are brought closer than a certain distance, they start repelling each other. In other words, a kind of spring effect takes place. As the potential U is related to the force by the relation $F = \frac{-dU}{dr}$, the resulting potential is a function of distance of separation (r). The variation of corresponding potential energy U (in eV) with distance r (in Å) is shown in figure.

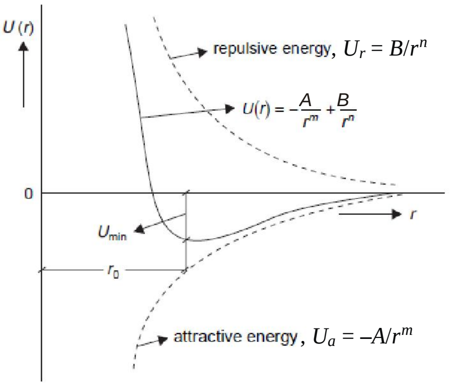
The attractive force gives rise to a negative potential and the repulsive force gives rise to a positive potential shown by dotted curves. The resultant potential energy is shown by full line curve. It has a minimum at a distance r_0 and represents the equilibrium position, where the attractive and the repulsive forces balance each other and potential energy has a maximum negative value. The potential energy $U(r_0)$ at distance r_0 is thus responsible for keeping the atoms bound in a solid and gives the cohesive or bonding energy of the solid.

The potential energy $U(r_0)$ is a negative quantity. The positive quantity $-U(r_0) = D$ is called the dissociation energy of the molecule.

The cohesive energy of a solid is defined as the energy which will be given out in the process of the formation of a crystal by bringing neutral atoms from infinity to the position of equilibrium separation.

If the potential energy due to attraction U_a is supposed to vary as the reciprocal of m^{th} power of the distance and that due to repulsion U_r as n^{th} power of $1/r$, then

$$U_a \propto \frac{1}{r^m} \Rightarrow U_a = -\frac{A}{r^m} \quad \text{and} \quad U_r \propto \frac{1}{r^n} \Rightarrow U_r = \frac{B}{r^n}$$



Therefore, resultant potential or cohesive energy,

$$U = U_a + U_r = -\frac{A}{r^m} + \frac{B}{r^n}$$

where, A and B are constants of proportionality. The cohesive enegy is generally expressed in eV per atom.

The force between the two atoms is given by

$$F = \frac{-dU}{dr} = \frac{mA}{r^{m+1}} - \frac{nB}{r^{n+1}}$$

At $r = r_0$ the attractive and repulsive forces balance each other and $F(r_0) = 0$. In other words at $r = r_0$, we get

$$\frac{mA}{r_0^{m+1}} - \frac{nB}{r_0^{n+1}} = 0 \qquad \Rightarrow \frac{m}{n} = \frac{B}{A} \cdot r_0^{m-n}$$

$$\Rightarrow r_0^{m-n} = \frac{A}{B} \cdot \frac{m}{n} \qquad \text{... (i)}$$

Hence, the potential energy at the equilibrium separation r_0 becomes

$$U(r_0) = \frac{-A}{r_0^m} + \frac{B}{r_0^n} = \frac{-A}{r_0^m}\left(1 - \frac{B}{A} r_0^{m-n}\right) = \frac{-A}{r_0^m}\left(1 - \frac{m}{n}\right)$$

Although the attractive and repulsive forces are in equilibrium at $r = r_0$, the potential energy is not zero as $m \neq n$. If $n >> m$ the total energy is essentially the energy of attraction given by $-\frac{A}{r_0^m}$.

For the potential energy to have a minimum at $r = r_0$ we have $\left.\frac{d^2U}{dr^2}\right|_{r=r_0} > 0$, i.e. it must be positive.

Now, $$\left[\frac{d^2U}{dr^2}\right]_{r=r_0} = \frac{-m(m+1)A}{r_0^{m+2}} + \frac{n(n+1)B}{r_0^{n+2}} > 0$$

$$\Rightarrow \qquad Bn(n+1)\, r_0^{m+2} > Am(m+1)\, r_0^{n+2}$$

$$\Rightarrow \qquad Bn(n+1) > Am(m+1)\, r_0^{n-m}$$

$$\Rightarrow \qquad Bn(n+1)\, r_0^{m-n} > Am(m+1)$$

Substituting the value of r_0 from (i), we have

$$Bn(n+1)\, \frac{A}{B} \cdot \frac{m}{n} > Am(m+1)$$

$$\Rightarrow \qquad n+1 > m+1$$

$$\Rightarrow \qquad n > m$$

In other words, a minimum in the energy curve is possible only if $n > m$. Thus the formation of a chemical bond requires that the repulsive forces should be of shorter range than the attractive forces.

The energy $U(r_0)$ at the equilibrium distance r_0 is called the binding energy, the energy of cohesion or dissociation energy of the molecule. This much energy is required to separate the atoms of a diatomic molecule to an infinite distance apart.

The cohesive energy may also be defined as the energy released when two atoms are brought close to each other at the equilibrium distance r_0.

Larger the energy released, more stable is the bond formed and hence more stable is the crystal structure.

Binding or cohesive energy of ionic crystals:

The calculation of binding or cohesive energy of crystals is one of the major problems of the theory of solids and requires the knowledge of constituents of the given crystal. For ionic crystals the calculation is simple and in further sections we will describe the calculation of binding energy of NaCl crystal.

The calculation of binding energy of ionic crystal was first given by Born and Madelung and later it was modified by Born and Mayer.

The calculation is based on the assumption that each ionic crystal is composed of positive and negative ions. Each of the ions have a spherical symmetric distribution as in rare gas atoms. Thus, it can be concluded that the force between the ions depends on the distance between the ions and is independent of the direction of approach. The force between ions is assumed to be electrostatic in nature. Thus the main contribution to the binding energy arises from electrostatic interaction and is called as Madelung energy.

In ionic crystal there exist two types of interactions, one is long range Coulomb's electrostatic interaction which may be either attractive or repulsive, and the other is short range repulsive interaction.

The Coulomb energy of attraction between two ions seperated by a distance r is

$$U_a = -\frac{e^2}{4\pi\varepsilon_0 r} \qquad \text{... (1)}$$

In the crystal, each ion interacts with all its neighbouring ions of the same sign as well as those of opposite signs. To take this into account, the net energy of attraction of one ion due to all other ions present in the crystal is written as

$$U_a = \frac{-\alpha e^2}{4\pi\varepsilon_0 r} \qquad \text{... (2)}$$

Where, α is the correction factor, called as Madelung constant. For simple crystals α lies between 1.6 and 1.8. For NaCl crystal, α = 1.7475 and for CsCl crystal, α =1.7626.

Now, in an ionic crystal as two ions approach each other under Coulomb attraction, at a certain distance apart, they begin to repel each other with a force which rises very rapidly with decrease in distance.

$$\therefore \qquad U_r = \frac{B}{r^n} \qquad \text{... (3)}$$

$\therefore$ The total potential energy $U = U_a + U_r = -\alpha\frac{e^2}{4\pi\varepsilon_0 r} + \frac{B}{r^n}$ ... (4)

At equilibrium distance $r = r_0$, U_r will be minimum.

$$\therefore \qquad \left.\frac{dU}{dr}\right|_{r=r_0} = 0 = \frac{\alpha e^2}{4\pi\varepsilon_0 r_0^2} - \frac{nB}{r_0^{n+1}}$$

$$\Rightarrow \qquad B = \frac{\alpha e^2}{4\pi\varepsilon_0 n} r_0^{n-1}$$

$$\therefore \qquad U|_{r=r_0} = -\frac{\alpha e^2}{4\pi\varepsilon_0 r_0} + \frac{\alpha e^2}{4\pi\varepsilon_0 r_0 n} = \frac{-\alpha e^2}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right) \qquad \text{... (5)}$$

Example: Assume that the energy of the two particles in the field of each other is given by $U(r) = -\frac{\alpha}{r} + \frac{\beta}{r^8}$ where α and β are cosntants and r is the distance between the centres of particles. In stable configuration, the ratio of energy of attraction to the energy of repulsion will be

(a) 6 (b) 8 (c) 4 (d) 2

Soln. $U(r) = -\frac{\alpha}{r} + \frac{\beta}{r^8}$

Force, $F = -\frac{dU}{dr} = -\left[\frac{\alpha}{r^2} - \frac{8\beta}{r^9}\right]$

For stable configuration, $F = 0$ at $r = r_0$

$$\Rightarrow \qquad \frac{\alpha}{r_0^2} = \frac{8\beta}{r_0^9} \Rightarrow r_0 = \left(\frac{8\beta}{\alpha}\right)^{1/7}$$

$$E_1 = \text{Energy of attraction } = +\frac{\alpha}{r_0} = +\frac{\alpha}{\left(\frac{8\beta}{\alpha}\right)^{1/7}}$$

$$E_2 = \text{Energy of repulsion } = \frac{\beta}{r_0^8} = \frac{\beta}{\left(\frac{8\beta}{\alpha}\right)^{8/7}} \Rightarrow \frac{E_1}{E_2} = \frac{\alpha \cdot \left(\frac{8\beta}{\alpha}\right)^{8/7}}{\left(\frac{8\beta}{\alpha}\right)^{1/7} \cdot \beta} = \frac{\alpha\left(\frac{8\beta}{\alpha}\right)}{\beta} = 8$$

Correct option is (b)

Example: Consider a gaseous molecule A^+B^- where the first ionisation energy of A is 502 kJ/mol, electron affinity for B atom is 335 kJ/mol and interionic ($A^+ - B^-$) separation is 3Å. The bond dissociation energy and comments on the stability of the molecule will be

(a) –296 kJ/mol and molecule will be stable (b) –296 kJ/mol and molecule will be unstable

(c) 296 kJ/mol and molecule will be stable (d) 296 kJ/mol and molecule will be unstable

Soln. From the expression of potential energy

$$U_e = -\frac{e^2}{4\pi \in_0 r} = \frac{-\left(1.6\times10^{-19}\right)^2 \times 9\times10^9}{3\times10^{-10}} = -7.68\times10^{-19} \text{ J/ion pair}$$

$$= -7.68\times10^{-19}\times6.023\times10^{23} \text{ J/mol} = -463 \text{ kJ/mol}$$

Bond dissociation energy is given by

$$D.E. = U_e + I.E. - E.A. = -463 + 502 - 335 = -296 \text{ kJ/mol}$$

Since, the bond dissociation energy is negative, the molecule A^+B^- will be stable (Negative implies attractive energy)

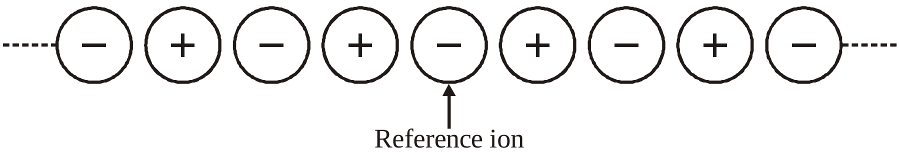
Correct option is (a)

Madelung constant: Madelung constant is the correction factor in the calculation of lattice energy of an ionic crystal when only nearest neighbours are considered for the calculation of energy.

Madelung constant for one-dimensional chain of ionic crystal:

Consider the simplest case of a one-dimensional crystal consisting of alternate positive and negative ions with interionic distance r_0. The electrostatic energy of the ionic crystal system is given by

$$\begin{aligned} U = E = &\text{ Electrostatic energy due to } 1^{\text{st}} \text{ nearest neighbours} \\ &+ \text{Electrostatic energy due to } 2^{\text{nd}} \text{ nearest neighbours} \\ &+ \text{Electrostatic energy due to } 3^{\text{rd}} \text{ nearest neighbours} \\ &+ ----\text{so on.} \end{aligned}$$



One-dimensional ionic crystal consisting of alternate positive and negative ions.

For example, in one-dimensional chain of NaCl crystal, each Na^+ ion has two nearest neighbour Cl^- ions at distance r_0, two second nearest neighbour Na^+ ions at distance $2r_0$, two third-nearest neighbour Cl^- ions at distance $3r_0$, so on. Similarly, each Cl^- ion has two nearest neighbour Na^+ ions at distance r_0, two second nearest neighbour Cl^- ions at distance $2r_0$, two third-nearest neighbour Na^+ ions at distance $3r_0$, so on.

Therefore, $$U = E = \frac{-2e^2}{4\pi\varepsilon_0(r_0)} + \frac{2e^2}{4\pi\varepsilon_0(2r_0)} + \frac{-2e^2}{4\pi\varepsilon_0(3r_0)} + \frac{2e^2}{4\pi\varepsilon_0(4r_0)} + - - -$$

$$= \frac{-2e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - - - -\right)$$

$$= \frac{-2e^2}{4\pi\varepsilon_0 r_0}\cdot\left[\ln(1+1)\right] = -\frac{e^2}{4\pi\varepsilon_0 r_0}(2\ln 2) = -\frac{e^2}{4\pi\varepsilon_0 r_0}\alpha \quad \left[\begin{array}{l}\because\ \ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \cdots \\ \text{Here, } x = 1\end{array}\right]$$

Here we have, $\alpha = 2\ln 2 = \text{Madelung constant}$. Hence for one dimensional chain of ionic crystal the Madelung constant is 2 ln2 or 1.3862.

Madelung constant for three-dimensional chain of ionic crystals:

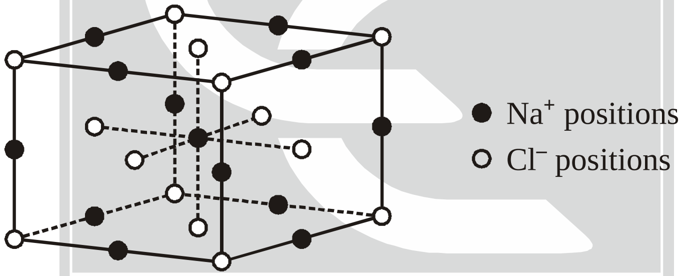
The calculation of Madelung constant for the three dimensional ionic crystal is not so simple. It is very difficult to write the successive terms by a casual inspection and the series converges slowly. Let's us take an example of NaCl crystal. The electrostatic energy of the NaCl crystal system is given by

$U = E =$ Electrostatic energy due to 1$^{\text{st}}$ nearest neighbours

+ Electrostatic energy due to 2$^{\text{nd}}$ nearest neighbours

+ Electrostatic energy due to 3$^{\text{rd}}$ nearest neighbours

$+ - - - -$ so on.



Equilibrium positions of ions in sodium chloride crystal

For three dimensional NaCl crystals, each Na$^+$ ion has 6 nearest neighbour Cl$^-$ ions, 12 second nearest neighbour Na$^+$ ions, 8 third-nearest neighbour Cl$^-$ ions, and so on. Similarly, each Cl$^-$ ion has 6 nearest neighbour Na$^+$ ions, 12 second nearest neighbour Cl$^-$ ions, 8 third-nearest neighbour Na$^+$ ions, and so on.

Therefore, $$U = E = \frac{-6e^2}{4\pi\varepsilon_0(r_0)} + \frac{12e^2}{4\pi\varepsilon_0(\sqrt{2}r_0)} + \frac{-8e^2}{4\pi\varepsilon_0(\sqrt{3}r_0)} + \frac{6e^2}{4\pi\varepsilon_0(\sqrt{4}r_0)} + - - -$$

$$= \frac{-e^2}{4\pi\varepsilon_0 r_0}\left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + - - - - -\right) = \frac{-\alpha e^2}{4\pi\varepsilon_0 r_0}$$

Here, $\alpha = 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + - - - - - = 1.7475$ is the Madelung constant for NaCl crystal.

SOLVED PROBLEMS

1. The energy of two particles in the field of each other at a separation r is given by $U = -\frac{\alpha}{r} + \frac{\beta}{r^8}$, where, α and β are constants. At what separation they will form a stable compound?

(a) $\left(\frac{8\beta}{\alpha}\right)^{1/7}$ (b) $\left(\frac{8\beta}{\alpha}\right)^{2/7}$ (c) $\left(\frac{4\beta}{\alpha}\right)^{1/7}$ (d) $\left(\frac{4\beta}{\alpha}\right)^{2/7}$

Soln. The energy of two particles in the field of each other at a separation r is given by $U = -\frac{\alpha}{r} + \frac{\beta}{r^8}$.

They will form a stable compound at a separation r_0 such that at that separation the energy U is a minimum, i.e.

$$\left.\frac{dU}{dr}\right|_{r=r_0} = 0 \quad \Rightarrow \quad \frac{dU}{dr} = \frac{\alpha}{r^2} - \frac{8\beta}{r^9}$$

$$\Rightarrow \quad \left.\frac{dU}{dr}\right|_{r=r_0} = \frac{\alpha}{r_0^2} - \frac{8\beta}{r_0^9} = 0 \quad \Rightarrow \quad \alpha = \frac{8\beta}{r_0^7} \quad \Rightarrow \quad r_0^7 = \frac{8\beta}{\alpha} \quad \Rightarrow \quad r_0 = \left(\frac{8\beta}{\alpha}\right)^{1/7}$$

Correct option is (a)

2. The energy of two particles in the field of each other is given by $U = -\frac{\alpha}{r^2} + \frac{\beta}{r^{10}}$, where α and β are constants and r is the separation between the particles. Determine the separation between the particles for a stable compound and also determine the cohesive energy of crystal.

(a) $-\frac{2}{5}\left(\frac{\alpha}{r_0^2}\right)$ (b) $-\frac{4}{5}\left(\frac{\alpha}{r_0^2}\right)$ (c) $-\frac{1}{5}\left(\frac{\alpha}{r_0^2}\right)$ (d) $\frac{1}{5}\left(\frac{\alpha}{r_0^2}\right)$

Soln. The energy of the two particles in the field of each other at a separation r is given by

$$U = -\frac{\alpha}{r^2} + \frac{\beta}{r^{10}} \qquad \text{... (i)}$$

They will form a stable compound at a separation r_0 such that at that separation the energy U is minimum i.e.,

$$\left.\frac{dU}{dr}\right|_{r=r_0} = 0 \quad \Rightarrow \frac{dU}{dr} = \frac{2\alpha}{r^3} - \frac{10\beta}{r^{11}} = 0 \quad \Rightarrow \quad r^8 = \frac{5\beta}{\alpha}$$

Therefore, separation for a stable compound $r_0 = \left(\frac{5\beta}{\alpha}\right)^{1/8}$.

Putting the value of $r = r_0$ in equation (i), we have

$$U_{\min} = -\alpha\left(\frac{\alpha}{5\beta}\right)^{1/4} + \beta\left(\frac{\alpha}{5\beta}\right)^{5/4} = \frac{\alpha^{5/4}}{(5\beta)^{1/4}}\left(\frac{\beta}{5\beta} - 1\right) = -\frac{4}{5}\left(\frac{\alpha^{5/4}}{(5\beta)^{1/4}}\right)$$

$$= -\frac{4\alpha}{5}\left(\frac{\alpha}{5\beta}\right)^{1/4} = -\frac{4\alpha}{5r_0^2} = -\frac{4}{5}\left(\frac{\alpha}{r_0^2}\right)$$

Therefore, cohesive energy of the crystal $U_{\min} = -\frac{4}{5}\left(\frac{\alpha}{r_0^2}\right)$.

Correct option is (b)

PRACTICE SET

1. The potential energy of a diatomic molecule in terms of interatomic distance R is given by

$$U(R) = -\frac{A}{R^m} + \frac{B}{R^n}$$

where A, B, m and n are constants. The equilibrium separation R_e is obtained as

(a) $\left(\frac{nA}{mB}\right)^{\frac{1}{(n-m)}}$ (b) $\left(\frac{nA}{mB}\right)^{\frac{1}{(m-n)}}$ (c) $\left(\frac{nB}{mA}\right)^{\frac{1}{(m-n)}}$ (d) $\left(\frac{nB}{mA}\right)^{\frac{1}{(n-m)}}$

2. The potential energy of a diatomic molecule in terms of interatomic separation R is given by

$$U(R) = -\frac{\alpha}{R^4} + \frac{\beta}{R^{12}}$$

The equilibrium separation is obtained as

(a) $\left(\frac{3\beta}{\alpha}\right)^{1/8}$ (b) $\left(\frac{3\beta}{\alpha}\right)^{1/6}$ (c) $\left(\frac{3\beta}{\alpha}\right)^{1/4}$ (d) $\left(\frac{3\beta}{\alpha}\right)^{1/2}$

3. The Madelung constant A for an infinite linear chain of ions of alternating charge at an equilibrium separation R_e is

(a) 0.3863 (b) 1.3863 (c) 2.3863 (d) 3.3863

4. The potential energy of two particles in stable configuration (at equilibrium) with $m = 2$ and $n = 10$ is equal to

(a) $-\frac{1}{5}\left(\frac{A}{R_e^2}\right)$ (b) $-\frac{2}{5}\left(\frac{A}{R_e^2}\right)$ (c) $-\frac{3}{5}\left(\frac{A}{R_e^2}\right)$ (d) $-\frac{4}{5}\left(\frac{A}{R_e^2}\right)$

5. The Madelung constant for an infinite array of two dimensional ionic charge distribution (i.e. two dimensional NaCl crystal) with equilibrium ion separation as R_e is

(a) 1.6135 (b) 2.6135 (c) 3.6135 (d) 4.6135

6. The potential energy of a diatomic molecule in terms of interatomic distance R is given by

$$U(R) = -\frac{A}{R^m} + \frac{B}{R^n}$$

where A, B, m and n are constants characteristics of the MX-molecules. Attractive and repulsive exponents are related through

(a) $n \ll m$ (b) $n < m$ (c) $n > m$ (d) $n \gg m$

ANSWER KEY

1. (d) **2. (a)** **3. (b)** **4. (d)** **5. (a)** **6. (c)**